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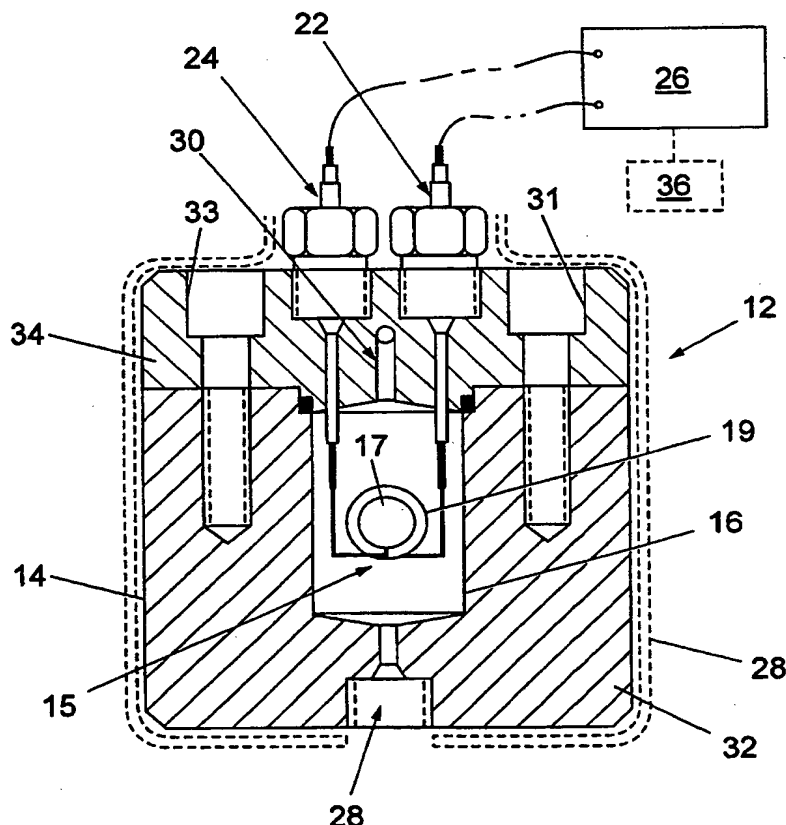
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(54) Title: CLATHRATE HYDRATE DISSOCIATION POINT DETECTION AND MEASUREMENT

## (57) Abstract

Apparatus and method for detecting the formation and dissociation of gas or clathrate hydrates in a fluid. The apparatus used comprises a piezoelectric crystal sensor and a signal analyser. The crystal sensor has a deposition surface in contact with the fluid. Under a range of pressures and or temperatures the resonant frequency or an electrical parameter dependent on the resonant frequency of the piezoelectric sensor is measured. There is a step change in the resonant frequency which occurs upon the formation or dissociation of a clathrate hydrate on the deposition surface, so that the formation or dissociation of said clathrate hydrate may be detected.



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1 CLATHRATE HYDRATE DISSOCIATION POINT DETECTION AND  
2 MEASUREMENT

3

4 The present invention relates to the detection of the  
5 dissociation of clathrate hydrates and in particular,  
6 but not exclusively, to the measurement of pressures  
7 and corresponding temperatures at which clathrate  
8 hydrates are found to dissociate.

9

10 Clathrate hydrates of gases are formed when, under  
11 favourable temperature and pressure conditions, gas  
12 molecules become encapsulated in crystalline structures  
13 of water. The water forms a cage-like structure around  
14 guest molecules. Chlorine hydrates were first  
15 discovered in 1810 and following this many compounds  
16 which form clathrate hydrates have been identified. In  
17 1934 it was discovered that gas clathrate hydrates were  
18 causing blocking of natural gas transmission lines and  
19 for this reason research aimed at understanding and  
20 resolving this problem was initiated and continues  
21 today. Apart from being considered as a problem in the  
22 oil industry, clathrate hydrates are considered  
23 important for a number of reasons such as a potential  
24 source of energy, and for use in processes such as  
25 desalination and gas transportation.

1 Clathrate hydrates, especially in the oil industry, are  
2 often referred to as gas hydrates, or simply as  
3 hydrates. Gas hydrates of interest, particularly with  
4 respect to producing, transporting and processing of  
5 natural gas and petroleum fluids, are composed of water  
6 and the following eight guest molecules: methane,  
7 ethane, propane, isobutane, normal butane, nitrogen,  
8 carbon dioxide and hydrogen sulphide. Other guest  
9 molecules capable of forming clathrate hydrates include  
10 ethane, nitrous oxide, acetylene, vinyl chloride,  
11 methyl bromide, ethyl bromide, cyclopropane, methyl  
12 mercaptan, sulphur dioxide, argon, krypton, oxygen,  
13 xenon, trimethylene oxides and others. Clathrate  
14 hydrate formation is a possibility wherever water  
15 exists in the presence of such molecules, both  
16 naturally and artificially, at temperatures above 0°C  
17 and below 0°C, when pressure is elevated.

18  
19 It is primarily due to their crystalline, insoluble,  
20 non-flowing nature that hydrates have been of interest  
21 to industry. They are a source of problems, because  
22 they block transmission lines, plug Blow Out  
23 Preventers, jeopardize the foundations of deepwater  
24 platforms and pipelines, collapse tubing and casing,  
25 and foul process heat exchangers and expanders. Common  
26 methods of preventing hydrate formation are the  
27 regulation of pipeline water content, the use of  
28 special drilling mud compositions and the injection of  
29 Large quantities of methanol into pipelines. All these  
30 methods are costly and complex, so there is a need to  
31 know more about the likelihood of clathrate formation  
32 in a particular sample.

33  
34 The point (in terms of pressure and temperature) at  
35 which, in a system containing a clathrate hydrate, the  
36 hydrate dissociates is known as the dissociation point.

1 The pressure at which a clathrate hydrate dissociates  
2 at a given temperature is referred to as the  
3 dissociation pressure (DP) for that temperature, while  
4 the temperature at which the hydrate dissociates for a  
5 given pressure is referred to as the dissociation  
6 temperature (DT) for that pressure. The DP and DT are  
7 important factors to be determined in order to identify  
8 and characterise the nature and properties of any  
9 clathrate hydrate.

10

11 Previously, the DP or DT of a given hydrate has been  
12 determined using methods dependent on visual  
13 identification of clathrate formation/dissociation,  
14 which are prone to human error and are inherently  
15 inaccurate. Measurements of the DT have also been made  
16 by mixing a test fluid with water, supercooling the  
17 mixture till the clathrate is formed, and then slowly  
18 warming the clathrate and detecting and/or measuring  
19 the increase in pressure which results from gas  
20 molecules escaping from inside the clathrate upon its  
21 dissociation. The latter method suffers from the  
22 problem of being extremely time consuming since the  
23 time taken for a system containing a sufficiently large  
24 sample of the (solid phase) clathrate to reach  
25 equilibrium at each desired temperature measurement is  
26 significant, in some cases a number of weeks.

27

28 It is an aim of the present invention substantially to  
29 avoid or minimise one or more of the foregoing  
30 disadvantages.

31

32 According to a first aspect of the present invention we  
33 provide an apparatus suitable for use in detecting the  
34 formation of, and/or the onset of dissociation of,  
35 clathrate hydrates, the apparatus comprising: a  
36 piezoelectric crystal sensor which is formed and

1 arranged to resonate at a variable frequency which is  
2 dependent upon a mass loading on a deposition surface  
3 thereof; and signal analyser means formed and arranged  
4 for monitoring, in use of the apparatus, directly or  
5 indirectly, change in the resonant frequency of the  
6 piezoelectric crystal sensor while one of the  
7 temperature and pressure of a test sample in contact  
8 with the deposition surface of the sensor is varied, so  
9 as to detect a substantial change in said resonant  
10 frequency occurring upon the formation or dissociation  
11 of a clathrate hydrate on the deposition surface,  
12 whereby the formation or dissociation of said clathrate  
13 hydrate may be detected.

14  
15 One advantage of the apparatus of the invention is that  
16 it enables the dissociation (or the formation) of  
17 clathrate hydrates to be detected very accurately.  
18 Unlike the aforementioned prior art, the invention does  
19 not rely on visual identification methods, or the  
20 detection of small pressure increases.

21  
22 According to a second aspect of the invention we  
23 provide an apparatus for measuring dissociation point  
24 temperatures and pressures of clathrate hydrates, the  
25 apparatus comprising: a piezoelectric crystal sensor  
26 which is formed and arranged to resonate at a variable  
27 frequency which is dependent upon a mass loading on a  
28 deposition surface thereof;  
29 a pressure vessel having a pressure chamber defined  
30 therein, said piezoelectric crystal sensor being  
31 mounted in the pressure chamber, and the pressure  
32 vessel having inlet means via which a test fluid may be  
33 introduced into the pressure chamber of the vessel;  
34 temperature control means for controlling the  
35 temperature in the pressure chamber;  
36 pressure control means for controlling the pressure in

1 the chamber;  
2 signal analyser means formed and arranged for  
3 monitoring, in use of the apparatus, directly or  
4 indirectly, change in the resonant frequency of the  
5 piezoelectric crystal while one of the temperature and  
6 pressure of test fluid in contact with the deposition  
7 surface of the sensor is varied, so as to detect a  
8 substantial change in said resonant frequency occurring  
9 upon the formation or dissociation of a clathrate  
10 hydrate on the deposition surface, whereby the  
11 formation or dissociation of said clathrate hydrate may  
12 be detected; and temperature measuring means and  
13 pressure measuring means for measuring the temperature  
14 and pressure in the chamber at least when the  
15 dissociation of said clathrate hydrate is detected.  
16

17 An advantage of the apparatus of present invention is  
18 that only a relatively small amount of the test fluid  
19 is required since only a small amount of clathrate  
20 hydrate need be formed in the apparatus of the  
21 invention in comparison with the prior art techniques  
22 which rely on visual identification of clathrate  
23 formation and dissociation, or detection of pressure  
24 changes due to clathrate hydrate  
25 formation/dissociation, and thus require much larger  
26 amounts of clathrate hydrates to be present. In  
27 consequence, another advantage of the apparatus is that  
28 it enables the DT or DP to be measured relatively  
29 quickly in comparison with the afore-mentioned prior  
30 art methods which required relatively large samples of  
31 clathrate hydrate (in which equilibrium conditions for  
32 a given temperature and pressure can take a very long  
33 time to reach) in order for effects occurring at the  
34 dissociation point to be detected.  
35

36 Said substantial change in the resonant frequency

1 occurring in the resonant frequency may be of the order  
2 of a few hundred to a few thousand Hertz. The  
3 magnitude of the change may be greater or smaller than  
4 this, though, depending on the amount of hydrate formed  
5 on the crystal and/or where on the crystal surface the  
6 hydrate is situated.

7  
8 Advantageously, the temperature and pressure measuring  
9 means are formed and arranged for continuously  
10 measuring temperature and pressure in the pressure  
11 chamber, in use of the apparatus.

12  
13 The piezoelectric crystal sensor preferably comprises a  
14 quartz crystal microbalance (QCM). The QCM  
15 conveniently comprises an AT-cut quartz crystal  
16 sandwiched between excitation electrodes to which a  
17 driving signal may be applied to generate a transverse  
18 shear wave across the thickness of the crystal. Such a  
19 QCM can be made to oscillate even when immersed in  
20 fluid (gas or liquid) and will resonate at a frequency  
21 which is dependent, among other things, on the mass  
22 loading on the crystal. Any change in the mass load on  
23 the crystal will change the resonant frequency of the  
24 QCM. When a clathrate hydrate forms from a mixture of  
25 ice and test fluid on the so-called deposition surface  
26 of the crystal, the mass load on the crystal will  
27 change significantly and this will, in turn,  
28 significantly change the resonant frequency of the QCM.  
29 Similarly, a significant change in the resonant  
30 frequency will occur when a clathrate hydrate present  
31 on the deposition surface of the crystal dissociates.

32  
33 A further advantage of the present invention is that  
34 if, due to a change in the structure of a clathrate  
35 hydrate being analysed, a density change in the hydrate  
36 occurs, the apparatus according to the invention may be



1 capable of detecting and measuring the point, in terms  
2 of pressure and temperature, at which this structural  
3 change takes place. Moreover, if more than one  
4 clathrate hydrate structures is formed on the  
5 deposition surface of the crystal, it may be possible  
6 to detect and/or measure the dissociation point  
7 temperature/pressure for each such structure.

8  
9 The signal analyser means is preferably adapted to  
10 control the driving signal supplied to the excitation  
11 electrodes and may be adapted to, for example, analyse  
12 the phase of an electrical impedance or gain of the  
13 sensor so as to detect a resonant condition of the  
14 sensor (occurring at a resonant frequency of the  
15 sensor). Similarly, the resonant condition could be  
16 detected by monitoring, for example, current, voltage  
17 or electrical conductance of the sensor so as to detect  
18 a resonant condition thereof. In use of the apparatus,  
19 the signal analyser means is advantageously adapted to  
20 produce and detect a resonant condition of the sensor  
21 at a predetermined number of different pressures, or  
22 temperatures, in the pressure chamber of the pressure  
23 vessel.

24  
25 The analyser means is preferably adapted to measure,  
26 and conveniently also to store or record, the value of  
27 the (driving) signal frequency, and/or one or more of  
28 the sensor current, voltage and conductance, at each  
29 detected resonant condition of the sensor. Change in  
30 the resonant frequency may thus be monitored directly,  
31 or alternatively indirectly by monitoring change in the  
32 values of, for example, current, voltage or  
33 conductance, at resonant frequency.

34  
35 Where the piezoelectric crystal sensor comprises a QCM,  
36 the quartz crystal incorporated therein is preferably

1 an unpolished quartz crystal. This had the advantage  
2 of increasing the likelihood that hydrate(s) which have  
3 formed will adhere to the crystal.

4  
5 In use of the apparatus, test fluid to be analysed is  
6 injected or other wise introduced into the pressure  
7 chamber so as to surround the piezoelectric crystal  
8 sensor. At least a small amount of water is preferably  
9 introduced onto said deposition surface of the crystal  
10 sensor and frozen prior to introduction of the test  
11 fluid to the pressure chamber, in order to allow  
12 clathrate hydrates to form. This water may be  
13 introduced by, for example, placing one or more drops  
14 of water onto the deposition surface of the crystal  
15 sensor and lowering the temperature in the pressure  
16 chamber so as to freeze the water. The pressure  
17 control means may conveniently comprise valve means on  
18 the inlet means of the pressure vessel for controlling  
19 the injection or release of fluid into or out of the  
20 pressure chamber. The pressure vessel may further  
21 include outlet means via which fluid contents of the  
22 pressure chamber may exit therefrom. Alternatively, or  
23 additionally, the pressure control means may comprise  
24 pump means for compressing or evacuating fluid in/form  
25 the pressure chamber. Pump means may be provided for  
26 connection to the outlet means, for evacuating the  
27 pressure chamber.

28  
29 The temperature control means may comprise a water  
30 jacket surrounding the pressure vessel. Additionally,  
31 or alternatively, the temperature control means may  
32 include a heat sink.

33  
34 The apparatus conveniently includes a pressure vessel  
35 mounting means incorporating a pivotal mounting for the  
36 pressure vessel, whereby the pressure vessel is

1 pivotally mounted to allow rotation of the vessel, in  
2 use of the apparatus, so as to mix the fluid contents  
3 of the vessel. Rotating the vessel can reduce the time  
4 taken for the contents of the pressure vessel to reach  
5 equilibrium.

6  
7 According to a third aspect of the invention we provide  
8 a method of measuring dissociation temperatures and  
9 dissociation pressures of a clathrate hydrate, the  
10 method comprising the steps of:

- 11 a) providing, in a pressure chamber of a pressure  
12 vessel, a piezoelectric crystal sensor which is formed  
13 and arranged to resonate at a variable frequency which  
14 is dependent on a mass loading on a deposition surface  
15 thereof;
- 16 b) depositing a small amount of water on said sensor  
17 deposition surface;
- 18 c) lowering the temperature in the pressure chamber  
19 below freezing so as to freeze said small amount of  
20 water;
- 21 d) evacuating the pressure chamber and subsequently  
22 introducing therein a test fluid;
- 23 e) controlling the temperature and pressure in the  
24 pressure chamber so as to achieve clathrate hydrate  
25 formation on the deposition surface of the sensor;
- 26 f) monitoring, directly or indirectly, change in the  
27 resonant frequency of the piezoelectric crystal sensor  
28 while said temperature and pressure are controlled, so  
29 as to detect a substantial change in said resonant  
30 frequency which occurs upon formation of said clathrate  
31 hydrate, thereby to detect the formation of said  
32 clathrate hydrate;
- 33 g) varying one of the temperature and pressure in the  
34 pressure chamber, preferably in a step-wise manner, so  
35 as to cause dissociation of the clathrate hydrate,  
36 while maintaining the other one of the temperature and

1 pressure substantially constant at a predetermined  
2 value;

3 h) monitoring, directly or indirectly, change in the  
4 resonant frequency of the piezoelectric crystal sensor  
5 while said one of the temperature and pressure is  
6 varied, so as to detect a substantial change in said  
7 resonant frequency which occurs upon dissociation of  
8 the clathrate hydrate, thereby to detect the  
9 dissociation of said clathrate hydrate; and

10 j) measuring the magnitude of the varying one of the  
11 temperature and pressure when the dissociation of said  
12 clathrate hydrate is detected, and the magnitude of the  
13 one of the temperature and pressure which is held  
14 substantially constant, the measured magnitudes  
15 representing one of: the dissociation temperature of  
16 said clathrate hydrate at a predetermined pressure, and  
17 the dissociation pressure of said clathrate hydrate at  
18 a predetermined temperature.

19  
20 Said small amount of water may be deposited on the  
21 sensor deposition surface in a number of possible ways.  
22 It is hereby expressly stated that steps (a) and (b) of  
23 the above method may be carried out in any order. For  
24 example, one or more drops of water may be placed on  
25 the deposition surface of the sensor prior to placing  
26 the sensor in the pressure chamber of the pressure  
27 vessel. Alternatively, water in the form of drops,  
28 mist, or liquid could be introduced into the pressure  
29 chamber once the sensor has been placed therein, as  
30 long as it can be ensured that at least some water will  
31 be deposited on the sensor deposition surface. The  
32 crystal may additionally be coated with a hygroscopic  
33 material for absorbing moisture introduced into the  
34 pressure chamber.

35

36 Using the above-described method, the dissociation

1 temperature (DT) at a given pressure, or alternatively  
2 the dissociation pressure (DP) at a given temperature,  
3 may be measured.

4  
5 Preferably, the temperature and pressure in the  
6 pressure chamber are continuously measured,  
7 conveniently throughout steps (c) to (j) of the method.

8  
9 The detection of said substantial change in the  
10 resonant frequency may be achieved by recording  
11 monitored values of the resonant frequency or, for  
12 example, current, voltage or conductance at resonant  
13 frequency, and the corresponding varying temperature or  
14 pressure values, in graphical form, thereby recording  
15 the substantial change in the resonant frequency, or  
16 the nominated other electrical property at resonant  
17 frequency, occurring at the DT or DP.

18  
19 The above-described apparatus and method(s) are  
20 intended in particular, but exclusively, for laboratory  
21 use. e.g. for the determination of dissociation  
22 temperatures and pressure of sample clathrate hydrates.  
23 It is envisaged that the apparatus could, nevertheless,  
24 be used in certain in situ applications, for example in  
25 monitoring applications where, for safety reasons or  
26 other operating considerations, the detection of the  
27 formation of clathrate hydrates is desirable. This  
28 could be the detection of the formation of clathrate  
29 hydrates in an underground gas pipe, for example,  
30 and/or measurement of the dissociation temperature or  
31 pressure of clathrate hydrates present in a system in  
32 which one of the temperature and pressure is varying  
33 while the other one remains substantially constant.

34  
35 Preferred embodiments of the invention will now be  
36 described by way of example only and with reference to

1 the accompanying drawings in which:  
2 Fig. 1(a) is a schematic side view (enlarged) of a  
3 quartz crystal microbalance (QCM);  
4 Fig. 1(b) is an end view of the arrangement of the  
5 quartz crystal and the electrodes of the QCM of  
6 Fig. 1(a);  
7 Fig. 2 is a schematic diagram of the equivalent  
8 electrical circuit representing the electrical  
9 behaviour of the QCM;  
10 Fig. 3 is a cross-sectional side view through an  
11 apparatus 12 according to the invention for detecting  
12 and measuring clathrate hydrate dissociation points;  
13 Fig. 4 shows graphs of resonant frequency vs.  
14 temperature, and conductance at resonant frequency  
15 versus temperature, obtained using the apparatus of  
16 Fig. 3, illustrating the dissociation of a clathrate  
17 hydrate formed from methane and isopentane, at  
18 8.28MPascals; and  
19 Fig. 5 is a graph of pressure vs. temperature at the  
20 hydrate phase boundary for ethane hydrate, comparing  
21 theoretical data with experimental data obtained using  
22 the apparatus of Fig. 3.  
23  
24 Fig. 1(a) shows schematically a typical Quartz Crystal  
25 Microbalance (QCM) 1. The QCM comprises an AT-cut  
26 polished quartz crystal 2 sandwiched between two gold  
27 excitation electrodes 3 (as shown in detail in  
28 Fig. 1(b)) that generate a transverse shear wave across  
29 the thickness of the quartz crystal (when a driving  
30 electrical signal is applied to the electrodes). The  
31 crystal 2 has an inherent resonant frequency at 5MHz.  
32 The crystal 2 is mounted by means of two connecting  
33 wires 6 connected to respective ones of the electrodes  
34 3, to a mounting base 4, as shown. Driving signals are  
35 applied to the connecting wires 6 via conducting pins 5  
36 which extend through the mounting base 4.

1 Fig. 2 shoes the elements of an equivalent electrical  
2 circuit 10 which the resonant electrical behaviour of  
3 the QCM imitates. As shown, the equivalent electrical  
4 circuit 10 comprises a resistor R, capacitor C and  
5 inductor L, all in series, which are in parallel with  
6 an additional capacitance  $C_0$  which is the static  
7 capacitance of the quartz crystal.

8  
9 Fig. 3 shows a cross-section through an apparatus 12  
10 according to a preferred embodiment of the invention.  
11 The apparatus 12 comprises a stainless steel pressure  
12 vessel 14 defining an internal pressure chamber 16 of  
13 volume 40 cubic centimetres (cc). A QCM 18 is mounted  
14 in the pressure chamber 16. The two electrodes 17  
15 (only one shown) of the QCM are gold, are bonded to the  
16 surface of the QCM crystal 19, and are connected, via  
17 high pressure vessel 14, to an HP 4194A impedance/gain  
18 phase analyser 26 (indicated in block form only)  
19 located remote from the pressure vessel. The pressure  
20 vessel has a sample inlet 28 communicating with the  
21 chamber 16 via which inlet test fluid may be introduced  
22 to the chamber 16. An outlet 30 is also provided in  
23 the pressure vessel via which fluids may exit from the  
24 chamber 16. The pressure vessel 14 is mounted on a  
25 pivot (not shown) to allow for rotation of the vessel,  
26 and thus mixing of the contents of the vessel, so as to  
27 help in achieving equilibrium of the contents of the  
28 pressure chamber 16. The pressure vessel 14 is also  
29 surrounded by a water jacket 28 (indicated in broken  
30 lines) for use in controlling the temperature of the  
31 contents of the pressure chamber 16. A temperature  
32 sensor (not shown) of the platinum resistance probe  
33 type is provided in the apparatus, in the water jacket  
34 28, for continuously monitoring the temperature of the  
35 water jacket (which is substantially the same, or  
36 closely approximates to, the temperature in the

1 pressure chamber). A pressure sensor (not shown) in  
2 the form of a strain gauge transducer is located in a  
3 branch off the outlet 30 of the pressure vessel and is  
4 arranged to continuously monitor the pressure therein.

5  
6 The pressure vessel 14, as shown in Fig. 3, in fact  
7 comprises two separate portions: a main portion 32  
8 having the inlet 28 and largely defining the chamber  
9 16, and a lid portion 34 having the electric feed  
10 throughs 22, 24, to which the QCM is attached, and the  
11 outlet 30. The lid portion 34 is bolted to the main  
12 portion 32, the recessed bolt holes 31, 33 being shown  
13 in Fig. 3. In use of the apparatus, a drop of water is  
14 placed on one surface of the quartz crystal 19,  
15 hereinafter referred to as "the deposition surface",  
16 prior to assembling the lid portion 34 to the main  
17 portion 32. After bolting the two portions of the  
18 pressure vessel together, thereby closing the chamber  
19 16 except to fluids entering or leaving therefrom via  
20 the inlet 28 and outlet 30 respectively, the  
21 temperature in the chamber 16 is lowered below 0°C,  
22 using the water jacket, in order to freeze the drop of  
23 water. The chamber 16 is then evacuated using a vacuum  
24 pump (not shown) connected to the outlet 30 and a  
25 sample of test fluids is then injected or pumped into  
26 the chamber 16 via the inlet 28. The chamber pressure  
27 P and temperature T are then adjusted using the water  
28 jacket and by releasing and/or injecting test fluid  
29 into or out of the chamber until conditions favourable  
30 for clathrate hydrate formation are achieved. The  
31 formation of such hydrates is obvious as it causes  
32 significant changes in the resonant frequency, or other  
33 electrical properties such as conductance at resonant  
34 frequency, which changes can be detected using the  
35 phase analyser 26.

36



1     Once the formation of clathrate hydrate(s) on the QCM  
2     has been detected, dissociation point measurements can  
3     then be obtained by, for example, raising the  
4     temperature step-wise in the chamber, while keeping the  
5     pressure therein substantially constant, and using the  
6     phase analyser 26 to monitor the resonant frequency,  
7     and/or conductance at resonant frequency, of the QCM at  
8     each temperature and to detect any significant changes  
9     therein, signalling dissociation of the clathrate  
10    hydrate. Alternatively, the temperature may be kept  
11    substantially constant while the pressure in the  
12    chamber is varied in a step-wise manner and the  
13    resonant frequency and/or conductance at resonant  
14    frequency is monitored.

15

16    Fig. 4 illustrates graphically the detection and  
17    measurement of the dissociation temperature, at 8.28  
18    MPascals pressure, for a clathrate hydrate formed from  
19    a mixture of methane and isopentane. The temperature  
20    in the chamber 16 was varied in a step-wise manner and  
21    at each temperature the resonant frequency  $f_r$  and the  
22    conductance at resonant frequency  $c_r$  of the QCM was  
23    measured by the phase analyser 26. By plotting a graph  
24    of resonant frequency  $f_r$  against pressure  $P$ , and/or a  
25    graph of Conductance  $c_r$  at resonant frequency against  
26    pressure  $P$ , the dissociation of the clathrate hydrate  
27    can be seen clearly in the graph as a significant  
28    change in the resonant frequency (a change of approx.  
29    2000Hz), and a significant change in the Conductance at  
30    resonant frequency (a change of approx. 550 $\mu$ S),  
31    occurring substantially at the dissociation temperature  
32    (approx. 284 Kelvin). Fig. 5 is a graph of pressure  $P$   
33    vs. temperature  $T$  plotted using theoretically  
34    calculated values for ethane hydrate in the region of  
35    the liquid/gas phase boundary. Experimental points  
36    obtained from the experimental data collected with the

1 apparatus of the invention are indicated on the graph  
2 in Fig. 5 and it can be seen that there is a good  
3 agreement between the theoretical and experimental  
4 data.

5  
6 In a further possible embodiment of the invention, the  
7 measurements of resonant frequency  $f_r$ , and Conductance  
8 at resonant frequency  $c_r$ , are recorded by a recording  
9 device 36 (e.g. a printer, or a microprocessor with a  
10 VDU) connected to the phase analyser 26, as shown in  
11 broken lines in Fig. 3.

12  
13 The invention has other applications, apart from those  
14 described above. The method of measuring the hydrate  
15 dissociation point of the present invention may be used  
16 for the rapid screening of chemicals for both hydrate  
17 inhibition and hydrate promotion. Tests were carried  
18 out with hydrates formed with methane and cyclopentane,  
19 and gave following results. Forming hydrates from  
20 water resulted in a drop in conductance of around 90  
21 micro Siemens. Forming hydrates from melting ice and  
22 from water with asphaltenes present gave a drop in  
23 conductance of around 476 micro Siemens. The drop is  
24 related to the conductance measurement when water or  
25 water with asphaltene is on the QCM with no hydrate  
26 formation. These results show that the formation of  
27 hydrates from melting ice or from water with  
28 asphaltenes is more efficient. This increase in  
29 efficiency is due to the number of nucleation sites in  
30 the droplet of water.

31  
32 The rate of drop in conductance measured in the method  
33 of the invention can also be used to show the rate of  
34 hydrate formation. The method and apparatus can be  
35 used to determine rapidly the efficiency of proposed  
36 hydrate inhibitors and/or promoters, using small

1 amounts of sample and with real fluids.

2

3 The small volume of sample needed represents a real  
4 advantage over prior art methods, which typically would  
5 need a sample of 50cc of fluid. The present invention  
6 can be carried out with a small sample, even a drop, on  
7 the surface of the crystal. The development of smaller  
8 crystal sensors will make the detection of hydrate  
9 dissociation points possible with samples whose mass is  
10 measured in nanograms.

11

12 Further tests with hydrates using the method of the  
13 invention have shown that where the cavity occupancy  
14 has an influence on the density of the hydrates formed,  
15 then this influence can be detected. For example, for  
16 hydrates formed from methane and isopentane, below the  
17 quintuple point structure H hydrates are formed,  
18 composed of water cages with methane and isopentane  
19 molecules filling the cavities. Above the quintuple  
20 point only structure I hydrates are formed with methane  
21 filling the cavities. There is a significant density  
22 difference between the two types of hydrates. By  
23 shifting the temperature and pressure above and below  
24 the quintuple point, the change in structure of the  
25 hydrates can be detected, since it results in a  
26 significant change in the conductance reading at  
27 resonant frequency.

28

29 The invention can find an application in the evaluation  
30 of surface treatments designed to prevent hydrates  
31 sticking.

32

33 These and other modifications and improvements can be  
34 incorporated without departing from the scope of the  
35 invention.

## 1 CLAIMS

2

3 1. An apparatus suitable for use in detecting the  
4 formation of, and/or the onset of dissociation of,  
5 clathrate hydrates, the apparatus comprising:

6 a piezoelectric crystal sensor which is formed and  
7 arranged to resonate at a variable frequency which is  
8 dependent upon a mass loading on a deposition surface  
9 thereof; and

10 signal analyser means formed and arranged for  
11 monitoring, in use of the apparatus, directly or  
12 indirectly, change in the resonant frequency of the  
13 piezoelectric crystal sensor while one of the  
14 temperature and pressure of a test sample in contact  
15 with the deposition surface of the sensor is varied, so  
16 as to detect a substantial change in said resonant  
17 frequency occurring upon the formation or dissociation  
18 of a clathrate hydrate on the deposition surface,  
19 whereby the formation or dissociation of said clathrate  
20 hydrate may be detected.

21

22 2. Apparatus according to Claim 1 further comprising:

23 a pressure vessel having a pressure chamber  
24 defined therein, said piezoelectric crystal sensor  
25 being mounted in the pressure chamber, and the pressure  
26 vessel having inlet means via which a test fluid may be  
27 introduced into the pressure chamber of the vessel.

28

29 3. Apparatus according to Claim 1 or 2 further  
30 comprising:

31 temperature control means for controlling the  
32 temperature in the pressure chamber.

33

34 4. Apparatus according to any preceding claim further  
35 comprising:

36 pressure control means for controlling the

1 pressure in the chamber.

2

3 5. Apparatus according to any preceding claim further  
4 comprising:

5 at least one of temperature measuring means and  
6 pressure measuring means for measuring the temperature  
7 and/or pressure in the chamber at least when the  
8 dissociation of said clathrate hydrate is detected.

9

10 6. Apparatus according to any preceding claim wherein  
11 the piezoelectric crystal sensor is an acoustic wave  
12 sensor selected from the group consisting of thickness-  
13 shear-mode (TSM) devices, surface-acoustic-wave (SAW)  
14 devices, acoustic-plate-mode (APM) devices and  
15 flexural-plate-wave (FPW) devices.

16

17 7. Apparatus according to Claim 6 wherein the  
18 piezoelectric crystal sensor is a quartz crystal  
19 microbalance comprising an AT-cut quartz crystal  
20 sandwiched between excitation electrodes to which a  
21 driving signal may be applied to generate a transverse  
22 shear wave across the thickness of the crystal.

23

24 8. Apparatus according to Claim 7 wherein the signal  
25 analyser means is adapted to control the driving signal  
26 supplied to the excitation electrodes.

27

28 9. Apparatus according to Claims 7 or 8 wherein the  
29 signal analyser means is adapted to analyse the phase  
30 of an electrical impedance or gain of the sensor so as  
31 to detect a resonant condition of the sensor which  
32 occurs at a resonant frequency of the sensor.

33

34 10. Apparatus according to Claim 9 wherein the  
35 resonant condition is detected by monitoring current,  
36 voltage or electrical conductance of the sensor.

1 11. Apparatus according to any preceding claim wherein  
2 the signal analyser means comprises control means  
3 adapted to produce and detect a resonant condition of  
4 the sensor at a predetermined number of different  
5 pressures, or temperatures, of the fluid in contact  
6 with the sensor.

7  
8 12. Apparatus according to any preceding claim wherein  
9 the signal analyser means comprises a driving signal  
10 generator and measurement means adapted to measure the  
11 frequency of the driving signal and/or one or more of  
12 the sensor current, voltage and conductance, at each  
13 detected resonant condition of the sensor.

14  
15 13. Apparatus according to Claim 12 wherein the signal  
16 analyser means comprises monitoring means adapted to  
17 monitor the change in the resonant frequency.

18  
19 14. Apparatus according to Claim 13 wherein said  
20 monitoring means monitors the change in resonant  
21 frequency by monitoring the change in the values of  
22 current, voltage or conductance, at resonant frequency.

23  
24 15. Apparatus according to any of Claims 12 to 14  
25 wherein the signal analyser means comprises data  
26 storage means for storing and/or recording the value of  
27 the driving signal frequency, and/or one or more of the  
28 sensor current, voltage and conductance, at each  
29 detected resonant condition of the sensor.

30  
31 16. Apparatus according to any preceding claim wherein  
32 the signal analyser means comprises computational means  
33 which recognises and calculates the point at which  
34 there is a discontinuity in the change of resonant  
35 frequency with changing temperature or changing  
36 pressure.

- 1 17. Apparatus according to Claim 16 wherein the  
2 discontinuity is a step change in the resonant  
3 frequency or a substantial change in the rate of change  
4 of resonant frequency with changing temperature or  
5 changing pressure.  
6
- 7 18. Apparatus according to any preceding claim wherein  
8 the piezoelectric crystal sensor comprises a quartz  
9 crystal having an unpolished quartz crystal surface, to  
10 promote the formation of crystals on said surface.  
11
- 12 19. Apparatus according to any preceding claim further  
13 comprising means for introducing a small amount of  
14 water onto said deposition surface of the crystal  
15 sensor.  
16
- 17 20. Apparatus according to any preceding claim further  
18 comprising valve means for controlling the injection or  
19 release of fluid into or out of the pressure chamber.  
20
- 21 21. Apparatus according to any preceding claim further  
22 comprising outlet means via which fluid contents of the  
23 pressure chamber may exit therefrom.  
24
- 25 22. Apparatus according to any preceding claim further  
26 comprising pump means for compressing or evacuating  
27 fluid in or from the pressure chamber.  
28
- 29 23. Apparatus according to any preceding claim further  
30 comprising a water jacket surrounding the pressure  
31 vessel.  
32
- 33 24. Apparatus according to any preceding claim further  
34 comprising a heat sink.  
35
- 36 25. Apparatus according to any preceding claim wherein

1 the pressure chamber is pivotally mounted to allow  
2 rotation of the chamber, in use of the apparatus, so as  
3 to mix the fluid contents of the chamber.

4  
5 26. A method of measuring dissociation temperatures  
6 and dissociation pressures of a clathrate hydrate, the  
7 method comprising the steps of:

- 8 a) providing a piezoelectric crystal sensor which is  
9 formed and arranged to resonate at a variable frequency  
10 which is dependent on a mass loading on a deposition  
11 surface thereof;
- 12 b) introducing a test fluid into contact with the  
13 deposition surface of the sensor;
- 14 c) controlling the temperature and/or pressure of the  
15 test fluid so as to achieve clathrate hydrate formation  
16 on the deposition surface of the sensor;
- 17 d) monitoring, directly or indirectly, change in the  
18 resonant frequency of the piezoelectric crystal sensor  
19 while said temperature and/or pressure are controlled,  
20 so as to detect a substantial change in said resonant  
21 frequency which occurs upon formation of said clathrate  
22 hydrate, thereby to detect the formation of said  
23 clathrate hydrate;
- 24 e) varying one of the temperature and pressure in the  
25 pressure chamber, preferably in a step-wise manner, so  
26 as to cause dissociation of the clathrate hydrate,  
27 while maintaining the other one of the temperature and  
28 pressure substantially constant at a predetermined  
29 value;
- 30 f) monitoring, directly or indirectly, change in the  
31 resonant frequency of the piezoelectric crystal sensor  
32 while said one of the temperature and pressure is  
33 varied, so as to detect a substantial change in said  
34 resonant frequency which occurs upon dissociation of  
35 the clathrate hydrate, thereby to detect the  
36 dissociation of said clathrate hydrate; and



1     g)     measuring the magnitude of the varying one of the  
2     temperature and pressure when the dissociation of said  
3     clathrate hydrate is detected, and the magnitude of the  
4     one of the temperature and pressure which is held  
5     substantially constant, the measured magnitudes  
6     representing one of: the dissociation temperature of  
7     said clathrate hydrate at a predetermined pressure, and  
8     the dissociation pressure of said clathrate hydrate at  
9     a predetermined temperature.

10

11     27. Method according to Claim 26 wherein the crystal  
12     sensor is in a pressure chamber and the test fluid is  
13     introduced into the pressure chamber .

14

15     28. Method according to Claim 27 wherein the method  
16     includes the following steps before or after step a):  
17     a1) depositing a small amount of water on said sensor  
18     deposition surface;  
19     a2) lowering the temperature in the pressure chamber  
20     below freezing so as to freeze said small amount of  
21     water; and  
22     a3) evacuating the pressure chamber and subsequently  
23     introducing therein a test fluid.

24

25     29. Method according to Claim 27 or 28 wherein water  
26     in the form of drops, mist, or liquid is be introduced  
27     into the pressure chamber after the sensor has been  
28     placed therein.

29

30     30. Method according to one of Claims 27 to 29,  
31     wherein the crystal surface is coated with a  
32     hygroscopic material for absorbing moisture introduced  
33     into the pressure chamber.

34

35     31. Method according to one of Claims 26 to 30 in  
36     which the detection of said substantial change in

1 resonant frequency and/or rate of change of resonant  
2 frequency is achieved by recording monitored values of  
3 said resonant frequency.  
4

5 32. Method according to Claim 31 in which the  
6 detection of said substantial change in resonant  
7 frequency and/or rate of change of resonant frequency  
8 is achieved by recording monitored values of an  
9 electrical parameter dependent upon said resonant  
10 frequency, said parameter being selected from the group  
11 comprising current, voltage or conductance.  
12

13 33. Method according to any of claims 26 to 32 further  
14 comprising the step of measuring the magnitude of the  
15 varying one of the temperature and pressure when said  
16 significant change in resonant frequency and/or rate of  
17 change in resonant frequency occurs, and the magnitude  
18 of the other one of the temperature and pressure which  
19 is held substantially constant.  
20

21 34. Method according to Claim 33, wherein the  
22 dissociation temperature (DT) at a given pressure is  
23 calculated.  
24

25 35. Method according to Claim 33, wherein the  
26 dissociation pressure (DP) at a given temperature is  
27 calculated.  
28

29 36. Method according to any of Claims 26 to 35, in  
30 which there is used an apparatus according to any one  
31 of Claims 1 to 25.  
32

1 / 3

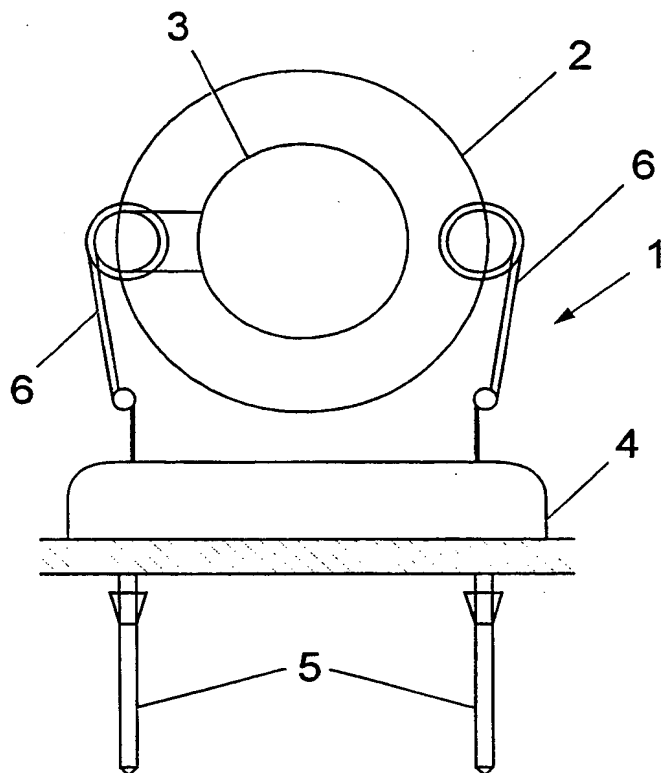


Fig. 1a

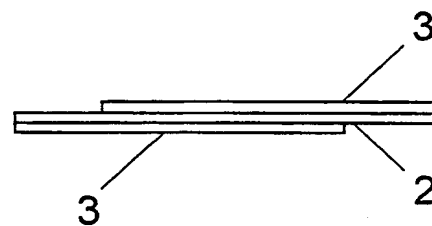


Fig. 1b

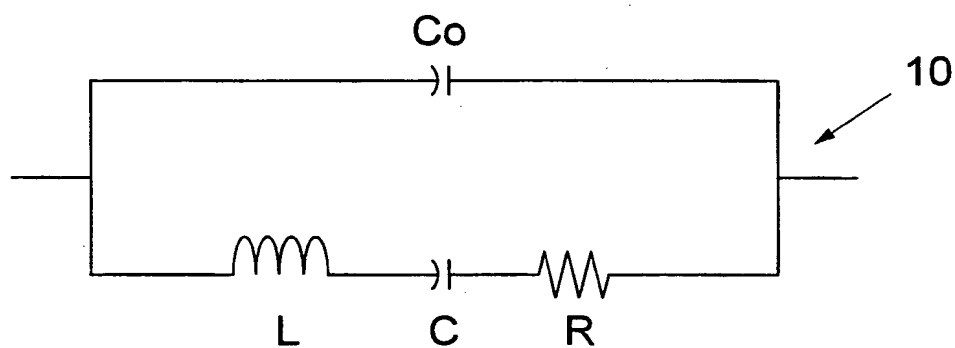


Fig. 2

2 / 3

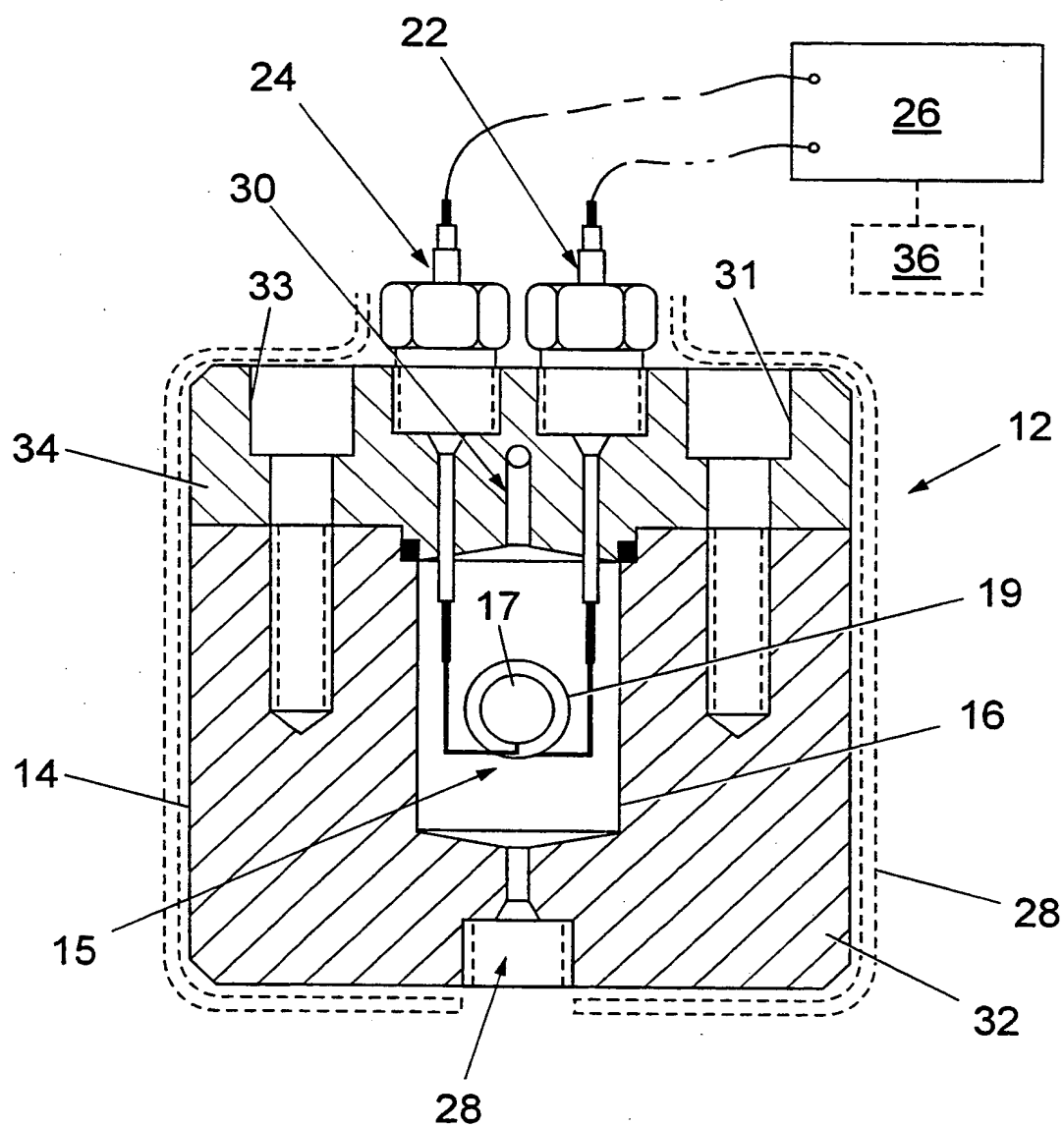


Fig. 3

SUBSTITUTE SHEET (RULE 26)

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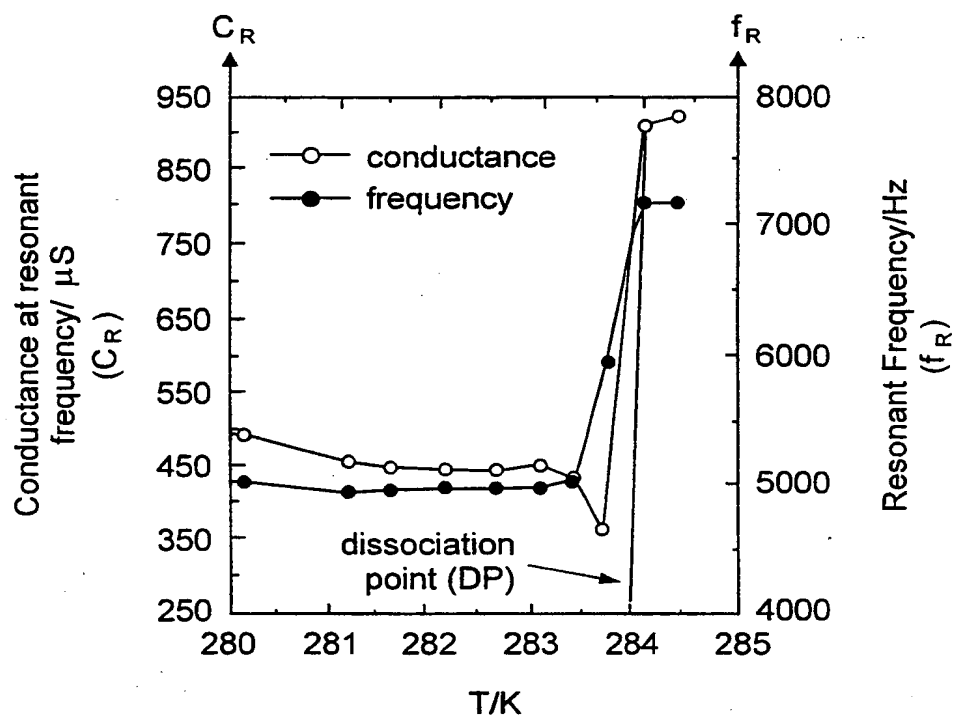


Fig. 4

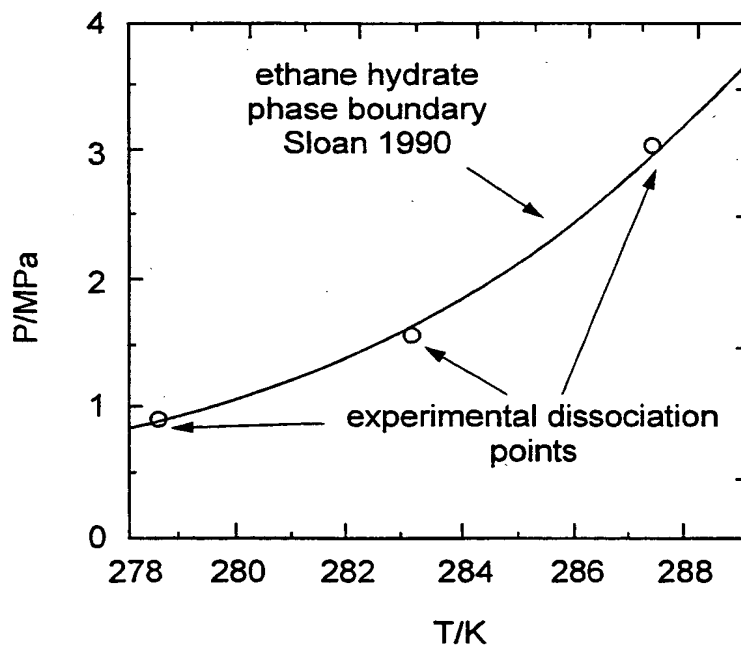


Fig. 5

SUBSTITUTE SHEET (RULE 26)

# INTERNATIONAL SEARCH REPORT

Int. National Application No  
PCT/GB 98/01005

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G01N27/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 187 980 A (BLAIR DIANNA S ET AL) 23 February 1993 see abstract	1,26
Y	<p style="text-align: center;">---</p> <p>G. D. HOLDER: "hydrate dissociation pressures of (methane + ethane + water) existence of a locus of minimum pressures" J. CHEM. THERMODYNAMICS, vol. 12, no. 7, 1980, LONDON, GB, pages 1093-1104, XP002071472 see page 1095, paragraph 3 - page 1097, paragraph 2; figure 1</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	1,26

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

14 July 1998

Date of mailing of the international search report

14/08/1998

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01005

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	A. DANESH: "hydrate equilibrium data of methyl cyclopentane with methane or nitrogen" TRANS. ICHM.E, vol. 72, no. a, 1994, pages 197-200, XP002071473 see page 197, right-hand column, last paragraph - page 199, left-hand column, paragraph 2; figures 1-3 ----	1
A	US 5 151 110 A (BRINKER CHARLES J ET AL) 29 September 1992 see abstract; figure 1A ----	1
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 173 (P-469), 18 June 1986 & JP 61 023955 A (MITSUBISHI DENKI KK), 1 February 1986, see abstract ----	1
A	ALFONSO L ET AL: "A QUARTZ CRYSTAL MICROBALANCE TO DETERMINE ENTHALPIES OF SUBLIMATION AT INTERMEDIATE TEMPERATURES BY THE KNUDSEN EFFUSION METHOD" MEASUREMENT SCIENCE AND TECHNOLOGY, vol. 5, no. 1, 1 January 1994, pages 51-54, XP000425430 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5187980 A	23-02-1993	NONE	
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		US 5224972 A	06-07-1993

Form PCT/ISA/210 (patent family annex) (July 1992)